

5 **PROCESS FOR THE MANUFACTURE OF DIESEL RANGE HYDROCARBONS**

Field of the invention

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The invention relates to an improved process for the manufacture of hydrocarbons, particularly diesel range hydrocarbons from bio oils and fats, wherein the formation of higher molecular weight compounds is reduced. The invention also relates to processing of feedstock containing free fatty acids, using
15 a high product recycle/fresh oil-ratio at reduced reaction temperatures.

Background of the invention

Environmental interests and an increasing demand for diesel fuel, especially in
20 Europe, encourage fuel producers to employ more intensively available renewable sources. In the manufacture of diesel fuels based on biological raw materials, the main interest has concentrated on vegetable oils and animal fats comprising triglycerides of fatty acids. Long, straight and mostly saturated hydrocarbon chains of fatty acids correspond chemically to the hydrocarbons present in diesel
25 fuels. However, neat vegetable oils display inferior properties, particularly extreme viscosity and poor stability and therefore their use in transportation fuels is limited.

Conventional approaches for converting vegetable oils or other fatty acid
30 derivatives into liquid fuels comprise transesterification, catalytic hydrotreatment, hydrocracking, catalytic cracking without hydrogen and thermal cracking among others. Typically triglycerides, forming the main component in vegetable oils, are converted into the corresponding esters by the transesterification reaction with an alcohol in the presence of catalysts. The obtained product is fatty acid alkyl ester,
35 most commonly fatty acid methyl ester (FAME). Poor low-temperature properties of FAME however limit its wider use in regions with colder climatic conditions.

5 Said properties are the result of the straight chain nature of the FAME molecule and thus double bonds are needed in order to create even bearable cold flow properties. Carbon-carbon double bonds and ester groups however decrease the stability of fatty acid esters, which is a major disadvantage of transesterification technology. Further, Schmidt, K., Gerpen J.V.: SAE paper 961086 teaches that the
10 presence of oxygen in esters results in undesirable higher emissions of NO_x, in comparison to conventional diesel fuels.

Undesired oxygen may be removed from fatty acids or their esters by deoxygenation reactions. The deoxygenation of bio oils and fats, which are oils
15 and fats based on biological material, to produce hydrocarbons suitable as diesel fuel products, may be carried out by catalytic hydroprocessing, such as hydrocracking, but also more controlled hydrotreating conditions may be utilized.

During hydrotreating, particularly hydrodeoxygenation oxygen containing groups
20 are reacted with hydrogen and removed through formation of water and therefore this reaction requires rather high amounts of hydrogen. Due to the highly exothermic nature of these reactions, the control of reaction heat is extremely important. Impure plant oil/fat or animal fat/oil, high reaction temperatures, insufficient control of reaction temperature or low hydrogen availability in the
25 feed stream may cause unwanted side reactions, such as cracking, polymerisation, ketonisation, cyclisation and aromatisation, and coking of the catalyst. These side reactions also decrease the yield and the properties of diesel fraction obtained.

Unsaturated feeds and free fatty acids in bio oils and fats may also promote the
30 formation of heavy molecular weight compounds, which may cause plugging of the preheating section and decrease catalyst activity and life.

The fatty acid composition, size and saturation degree of the fatty acid may vary considerably in feedstock of different origin. The melting point of bio oil or fat is
35 mainly a consequence of saturation degree. Fats are more saturated than liquid

5 oils and in this respect need less hydrogen for hydrogenation of double bonds. Double bonds in a fatty acid chain also promote different kinds of side reactions, such as oligomerisation/polymerization, cyclisation/aromatisation and cracking reactions, which deactivate catalyst, increase hydrogen consumption and reduce diesel yield.

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Plant oils/fats and animal oils/fat may contain typically 0-30% of free fatty acids, which are formed during enzymatic hydrolysis of triglycerides especially when oil seeds are kept in humid atmosphere. Free fatty acids can be also formed during purification of bio oils and fats, especially during caustic wash i.e. alkali catalyzed hydrolysis. The amount of free fatty acids present in plant/vegetable oils is typically 1-5 wt % and in animal fat 10-25 wt-%. Free fatty acids are corrosive in their nature, they can attack against materials of unit or catalyst and can promote some side reactions. Free fatty acids react very efficiently with metal impurities producing metal carboxylates, which promote side reaction chemistry.

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Fatty acids may also promote the formation of heavy compounds. The boiling range of these heavy compounds is different from the range of diesel fuel and may shorten the life of isomerisation catalyst. Due to the free fatty acids contained in bio oils and fats, the formation of heavy molecular weight compounds are significantly increased compared to triglyceridic bio feeds, which have only low amount of free fatty acids (<1%).

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Biological raw materials often contain metal compounds, organic nitrogen, sulphur and phosphorus compounds, which are known catalyst inhibitors and poisons inevitably reducing the service life of the catalyst and necessitating more frequent catalyst regeneration or change. Metals in bio oils/fats inevitably build up on catalyst surface and change the activity and selectivity of the catalyst. Metals can promote some side reactions, but blocking of catalyst active sites typically decreases the activity and thus metal impurities such as Na, Ca, and Mg compounds should be removed as efficiently as possible.

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5 Hydrolysis of triglycerides produces also diglycerides and monoglycerides, which are partially hydrolyzed products. Diglycerides and monoglycerides are surface-active compounds, which can form emulsions and make liquid/liquid separations of water and oil more difficult. Bio oils and fats can also contain other glyceride-like surface-active impurities like phospholipids (for example lecithin), which
10 have phosphorus in their structures. Phospholipids are gum like materials, which can be harmful for catalysts. Natural oils and fats also contain other types of components, such as waxes, sterols, tocopherols and carotenoids, some metals and organic sulphur compounds as well as organic nitrogen compounds. These compounds can be harmful for catalysts or pose other problems in processing.

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Patents US 4,992,605 and US 5,705,722 describe processes for the production of diesel fuel additives by conversion of bio oils into saturated hydrocarbons under hydroprocessing conditions with CoMo and NiMo catalysts. The process operates at high temperatures of 350-450°C and produces n-paraffins and other
20 hydrocarbons. The product has a high cetane number but poor cold properties (melting point >20°C), which limits the amount of product that can be blended in conventional diesel fuels in summer time and prevent its use during winter time. The formation of heavy compounds with a boiling point above 343°C was observed, especially when a fatty acid fraction was used as a feed. A reaction
25 temperature with a lower limit of 350°C was concluded as a requirement for trouble-free operation.

A two-step process is disclosed in FI 100248, for producing middle distillates from vegetable oil by hydrogenating fatty acids or triglycerides of vegetable oil
30 origin using commercial sulphur removal catalysts, such as NiMo and CoMo, to give n-paraffins, followed by isomerising said n-paraffins using metal containing molecular sieves or zeolites to obtain branched-chain paraffins. The hydrotreating was carried out at rather high reaction temperatures of 330-450°C, preferably 390°C. Hydrogenating fatty acids at those high temperatures leads to shortened
35 catalyst life resulting from coking and formation of side products.

- 5 EP 1 396 531 describes a process containing at least two steps, the first one being a hydrodeoxygenation step and the second one being a hydroisomerisation step utilizing counter-current flow principle, and using biological raw material containing fatty acids and/or fatty acid esters as the feedstock. The process comprises an optional stripping step.

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Deoxygenation of plant oils/fats and animal fats with hydrogen use a large amount of hydrogen and at the same time releases significant amount of heat. Heat is produced from deoxygenation reactions and from double bond hydrogenation. Different feedstocks produce significantly different amounts of reaction heat. The variation of reaction heat produced is mainly dependent on double bond hydrogenation. The average amount of double bonds per triglyceride molecule can vary from about 1.5 to more than 5 depending on the source of bio oil or fat.

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FR 2,607,803 describes a process for hydrocracking of vegetable oils or their fatty acid derivatives under pressure to give hydrocarbons and to some extent acid. The catalyst contains a metal dispersed on a support. A high temperature of 370°C did not result complete oxygen removal or high selectivity of n-paraffins. The product mixture formed, contained also some intermediate fatty acid compounds.

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- 25 Formation of water during hydrotreatment results from the deoxygenation of triglyceride oxygen by the means of hydrogen (hydrodeoxygenation). Deoxygenation under hydrodeoxygenation conditions is to some extent accompanied by a decarboxylation reaction pathway and a decarbonylation reaction pathway. Deoxygenation of fatty acid derivatives by decarboxylation and/or decarbonylation reactions forms carbon oxides (CO₂ and CO) and aliphatic hydrocarbon chains with one carbon atom less than in the original fatty acid molecule. Decarb-reactions mean here decarboxylation and/or decarbonylation reactions.

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- 5 The feasibility of decarboxylation varies greatly with the type of carboxylic acid or derivative thereof used as the starting material. Alpha-hydroxy, alpha-carbonyl and dicarboxylic acids are activated forms and thus they are more easily deoxygenated by decarb-reactions. Saturated aliphatic acids are not activated this way and generally are difficult to deoxygenate through decarb-reactions.

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Decarboxylation of carboxylic acids to hydrocarbons by contacting carboxylic acids with heterogeneous catalysts was suggested by Maier, W. F. et al: Chemische Berichte (1982), 115(2), 808-12. Maier et al tested Ni/Al₂O₃ and Pd/SiO₂ catalysts for decarboxylation of several carboxylic acids. During the
15 reaction the vapors of the reactant were passed through a catalytic bed together with hydrogen. Hexane represented the main product of the decarboxylation of the tested compound heptanoic acid. When nitrogen was used instead of hydrogen no decarboxylation was observed.

- 20 Patent US 4,554,397 discloses a process for the manufacture of linear olefins from saturated fatty acids or esters, suggesting a catalytic system consisting of nickel and at least one metal selected from the group consisting of lead, tin and germanium. With other catalysts, such as Pd/C, low catalytic activity and cracking to saturated hydrocarbons, or formation of ketones when Raney-Ni was used,
25 were observed.

Object of the invention

An object of the invention is an improved process for the manufacture of diesel
30 range hydrocarbons from bio oils and fats, with high selectivity, essentially without side reactions and with high diesel yield.

A further object of the invention is an improved process for the manufacture of diesel range hydrocarbons from bio oils and fats, wherein the extent of high

- 5 molecular weight compounds formed during hydrotreating is decreased and the stability of the catalyst is increased.

A still further object of the invention is an improved process for the manufacture of diesel range hydrocarbons from bio oils and fats, wherein the hydrotreatment of
10 triglyceride feedstock containing free fatty acids is carried out using dilution of fresh feed and reduced reaction temperature.

A still further object of the invention is an improved process for the manufacture of diesel range hydrocarbons from bio oils and fats, which process produces high
15 quality diesel component with high yield.

Characteristic features of the process according to the invention are provided in the claims.

20 **Definitions**

Here hydroprocessing is understood as catalytic processing of organic material by all means of molecular hydrogen.

25 Here hydrotreatment is understood as a catalytic process, which removes oxygen from organic oxygen compounds as water (hydrodeoxygenation, HDO), sulphur from organic sulphur compounds as dihydrogen sulphide (H_2S) (hydrodesulphurisation, HDS), nitrogen from organic nitrogen compounds as ammonia (NH_3) (hydrodenitrogenation, HDN) and halogens, for example chlorine
30 from organic chloride compounds as hydrochloric acid (HCl) (hydrodechlorination, HDCl), typically under the influence of sulphided NiMo or sulphided CoMo catalysts.

- 5 Here deoxygenation is understood to mean removal of oxygen from organic molecules, such as fatty acid derivatives, alcohols, ketones, aldehydes or ethers by any means previously described.

Here hydrodeoxygenation (HDO) of triglycerides or other fatty acid derivatives or
10 fatty acids is understood to mean the removal of carboxyl oxygen as water by the means of molecular hydrogen under the influence of catalyst.

Here decarboxylation and/or decarbonylation of triglycerides or other fatty acid derivatives or fatty acids is understood to mean removal of carboxyl oxygen as
15 CO₂ (decarboxylation) or as CO (decarbonylation) with or without the influence of molecular hydrogen. Decarboxylation and decarbonylation reactions either together or alone are referred to as decarb-reactions.

Here hydrocracking is understood as catalytic decomposition of organic
20 hydrocarbon materials using molecular hydrogen at high pressures.

Here hydrogenation means saturation of carbon-carbon double bonds by means of molecular hydrogen under the influence of a catalyst.

25 Here n-paraffins mean normal alkanes or linear alkanes that do not contain side chains.

Here isoparaffins mean alkanes having one or more C₁ – C₉ , typically C₁ - C₂ alkyl side chains, typically mono-, di-, tri- or tetramethylalkanes. .

30 The feed (total feed) to the hydrotreating unit is here understood to comprise fresh feed and at least one dilution agent.

5 Summary of the invention

The present invention relates to an improved process for the manufacture of hydrocarbons from renewable sources, such as plant oils/fats and animal oils/fats, comprising a hydrotreating step and an isomerisation step. Particularly the invention relates to the transformation of the starting materials comprising triglycerides, fatty acids and derivatives of fatty acids or combinations of thereof, into n-paraffins with reduced formation of high molecular weight hydrocarbons using dilution of fresh feed and reduced reaction temperature in the hydrotreating step and converting the obtained n-paraffins into diesel range branched alkanes using isomerisation, with high diesel yield. The hydrotreating step is carried out contacting the feed comprising fresh feed and at least one diluting agent with a hydrotreatment catalyst under hydrotreatment conditions. Then the obtained product is isomerised with an isomerisation catalyst under isomerisation conditions. The hydrocarbon oil formed via this process is a high quality diesel component.

Detailed description of the invention

It was surprisingly found that dilution of fresh feed in the hydrotreatment step, in combination with decreased reaction temperature reduces the undesired side reactions and improves reaction selectivity, particularly when a starting material containing free fatty acids is used. The diluting agent can be a hydrocarbon of biological origin and/or non-biological origin. The dilution agent can also be recycled product from the process (product recycle). The diluting agent / fresh feed-ratio is 5-30:1, preferably 10-30:1 and most preferably 12-25:1.

A preferable embodiment of the invention and of the hydrotreatment step is illustrated in Figure 1, wherein a hydrotreatment process configuration is provided, comprising one or more catalyst beds in series, hydrotreated product recycle introduction on the top of the first catalyst bed and fresh feed, quench liquid and hydrogen introduction on top of each catalyst beds. This results in

- 5 improved control of the reaction temperature in the catalyst beds and hence diminishes undesired side reactions.

In Figure 1 the hydrotreatment reactor 100 comprises two catalyst beds 10 and 20. Fresh feed 11 is introduced as streams 12 and 13 on the catalyst beds 10 and 20, respectively, and hydrogen as stream 22 and 23 on the catalyst beds 10 and 20, respectively. The fresh feed stream 12 is first mixed with the hydrotreated product recycle stream 41 and quench liquid stream 43 and the resulting mixture 31, diluted in the fresh feed concentration, is then introduced on the catalyst bed 10. In order to obtain a required sulphur concentration in the feed stream 31, required amount of sulphur make up is added to the fresh feed stream 11 via stream 15. As mixture 31 passes through the catalyst bed 10 with the hydrogen stream 22, fatty acids and fatty acid derivatives of the fresh feed stream 12 are converted to the corresponding reaction products. A two-phase stream 32 is withdrawn from the bottom of the catalyst bed 10 and is mixed with the fresh feed stream 13, quench liquid stream 44 and the hydrogen stream 23. The formed vapor-liquid mixture 33, diluted in the fresh feed concentration, is then introduced on the catalyst bed 20 at reduced temperature due to cooling effect of the hydrogen, quench liquid and fresh feed, passed through the catalyst bed 20 and finally withdrawn from the catalyst bed as a product stream 34. The stream 34 is separated in to a vapor stream 35 and liquid stream 36 in the high temperature separator 101. Vapor stream 35 is rich in hydrogen and is directed to further treatment. Part of the liquid stream 36 is returned to the reactor 100 as recycle stream 40, which is further divided to dilution stream 41 and total quench liquid stream 42. The quench liquid stream 42 is cooled in the heat exchanger 102 to provide adequate cooling effect on the top of the catalyst beds 10 and 20. Hydrotreated product stream 51 is directed from the hydrotreatment step to further processing.

The catalyst beds 10 and 20 may be located in the same pressure vessel or in separate pressure vessels. In the embodiment where the catalyst beds are in the same pressure vessels the hydrogen streams 22 and 23 may alternatively be

5 introduced on the catalyst bed 10 and then be passed through the catalyst beds 10 and 20. In the embodiment where the catalyst beds are in separate pressure vessels, the catalyst beds may operate in parallel mode with separate dilution streams, hydrogen streams and quench liquid streams. The number of catalyst beds may be one or two or more than two.

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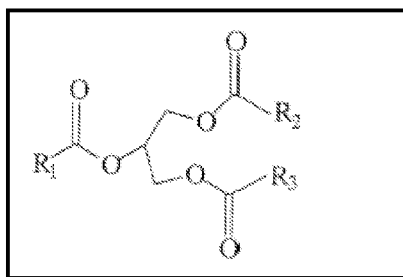
The sulphur make up to the hydrotreatment step may be introduced with the fresh feed stream 11. Alternatively, required amount of sulphur may be fed with the hydrogen streams 22 and 23 as gaseous sulphur compound such as hydrogen sulphide.

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Hydrogen is fed to the hydrotreating reactor in excess of the theoretical hydrogen consumption. During the hydrotreating step, triglyceride oils, fatty acids and derivatives thereof are almost theoretically converted to n-paraffins without or almost without side reactions. Additionally, propane is formed from the glycerol
20 part of the triglycerides, water and CO and/or CO₂ from carboxylic oxygen, H₂S from organic sulphur compounds and NH₃ from organic nitrogen compounds. Using the above described procedures in the hydrotreating step, the temperature needed for reactions to start up is achieved in the beginning of each catalyst bed, the temperature increase in the catalyst beds is limited, harmful and partially
25 converted product intermediates can be avoided and the catalyst life is extended considerably. The temperature at the end of the catalyst bed is controlled by net heat of reactions and to the extent of the dilution agent used. The dilution agent may be any hydrocarbon available, of biological origin or non-biological origin. It can also be recycled product from the process. Fresh feed content from feed (total
30 feed) is be less than 20 wt-%. If the product recycle is used, product recycle/fresh feed ratio is 5-30:1, preferably 10-30:1, most preferably 12-25:1. After the hydrotreatment step, the product is subjected to an isomerization step.

5 Feedstock

The bio oil and/or fat used as the fresh feed in the process of the present invention originates from renewable sources, such as fats and oils from plants and/or animals and/or fish and compounds derived from them. The basic structural unit of a typical plant or vegetable or animal oil/fat useful as the feedstock is a triglyceride, which is a triester of glycerol with three fatty acid molecules, having the structure presented in the following formula I:



Formula 1. Structure of triglyceride

In formula I R_1 , R_2 and R_3 are alkyl chains. Fatty acids found in natural triglycerides are almost solely fatty acids of even carbon number. Therefore R_1 , R_2 , and R_3 typically are $C_5 - C_{23}$ alkyl groups, mainly $C_{11}-C_{19}$ alkyl groups and most typically C_{15} or C_{17} alkyl groups. R_1 , R_2 , and R_3 may contain carbon-carbon double bonds. These alkyl chains can be saturated, unsaturated or polyunsaturated.

Suitable bio oils are plant and vegetable oils and fats, animal fats, fish oils, and mixtures thereof containing fatty acids and/or fatty acid esters. Examples of suitable materials are wood-based and other plant-based and vegetable-based fats and oils such as rapeseed oil, colza oil, canola oil, tall oil, sunflower oil, soybean oil, hempseed oil, olive oil, linseed oil, mustard oil, palm oil, peanut oil, castor oil, coconut oil, as well as fats contained in plants bred by means of gene manipulation, animal-based fats such as lard, tallow, train oil, and fats contained in milk, as well as recycled fats of the food industry and mixtures of the above.

- 5 Bio oil and fat suitable as fresh feed may comprise C₁₂ – C₂₄ fatty acids, derivatives thereof such as anhydrides or esters of fatty acids as well as triglycerides of fatty acids or combinations of thereof. Fatty acids or fatty acid derivatives, such as esters may be produced via hydrolysis of bio oils or by their fractionalization or transesterification reactions of triglycerides.

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- In order to avoid catalyst deactivation and undesired side reactions the feed shall comply with the following requirements: The amount of alkaline and alkaline earth metals, calculated as elemental alkaline and alkaline earth metals, in the feed is below 10, preferably below 5 and most preferably below 1 w-ppm. The amount
15 of other metals, calculated as elemental metals, in the feed is below 10, preferably below 5 and most preferably below 1 w-ppm. The amount of phosphorus, calculated as elemental phosphorus is below 30, preferably below 15 and most preferably below 5 w-ppm.

- 20 In many cases the feedstock, such as crude plant oil or animal fat, is not suitable as such in processing because of high impurity content and thus the feedstock is preferably purified using suitably one or more conventional purification procedures before introducing it to the hydrotreating step of the process. Examples of some conventional procedures are provided below:

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- Degumming of plant oils/fats and animal oils/fats means the removal of phosphorus compounds, such as phospholipids. Solvent extracted vegetable oils often contain significant amounts of gums, typically 0.5-3% by weight, which are mostly phosphatides (phospholipids) and therefore a degumming stage is needed
30 for crude plant oils and animal fats in order to remove phospholipids and metals present in crude oils and fats. Iron and also other metals may be present in the form of metal-phosphatide complexes. Even a trace amount of iron is capable of catalysing oxidation of the oil or fat.

- 5 Degumming is performed by washing the feed at 90-105 °C, 300-500 kPa(a), with H_3PO_4 , NaOH and soft water and separating the formed gums. A major amount of metal components, which are harmful for the hydrotreatment catalyst, are also removed from the feedstock during the degumming stage. The moisture content of the degummed oil is reduced in dryer at 90-105 °C, 5-50 kPa(a).

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- A feedstock, which is optionally degummed or refined in another conventional way, may be bleached. In the bleaching the degummed or refined feedstock is heated and mixed with natural or acid-activated bleaching clay. Bleaching removes various impurity traces left from other pretreatment steps like
15 degumming, such as chlorophyll, carotenoids, phospholipids, metals, soaps and oxidation products. Bleaching is typically carried out under vacuum to minimize possible oxidation. Generally the goal of bleaching is to reduce the color pigments in order to produce an oil of acceptable color and to reduce the oxidation tendency of oil.

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Optionally the triglyceride structures of the feedstock may be decomposed by prehydrogenating the double bonds using reduced reaction temperature with NiMo or other catalyst, prior to the of by hydrodeoxygenations in order to prevent double bond polymerisation of unsaturated triglycerides.

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- The process according to the invention is particularly advantageous when the fresh feed contains more than 5 % of free fatty acids and even more than 10 % of free fatty acids. Thus also naturally occurring fats and oils containing significant amounts of free fatty acids can be processed without the removal of free fatty
30 acids.

In the following the process according to the invention comprising a hydrotreating step and an isomerisation step is described in more detail.

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5 Hydrotreating of bio oils and fats

In the first step of the process, i.e. in the hydrotreating step, fatty acids, triglycerides and other fatty acid derivatives comprised in the feed are deoxygenated, denitrogenated and desulphurised.

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The feed comprises fresh feed and at least one dilution agent and the ratio of the dilution agent/fresh feed is 5 – 30:1, preferably 10-30:1, most preferably 12-25:1.

The dilution agent is selected from hydrocarbons and recycled product of the process i.e. product recycle or mixtures thereof.

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In the hydrotreating step, the pressure range may be varied between 20 and 150 bar, preferably between 50 and 100 bar, and the temperature between 200 and 400 °C, preferably between 250 and 350 °C and most preferably between 280 and 340°C.

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It was found that the selectivity of decarb-reactions and the deoxygenation through decarb-reactions can be promoted during hydrotreating over the hydrotreatment catalyst, by using sulphur content of 50 – 20000 w-ppm, preferably 1000-8000 w-ppm, most preferably 2000-5000 w-ppm of sulphur in the total feed, calculated as elemental sulphur. The specific sulphur content in the feed is able to double the extent of n-paraffins formed by removal of COx. Complete deoxygenation of triglycerides by decarb-reactions can theoretically lower the consumption of hydrogen about 60% (max) compared with pure deoxygenation by hydrogen.

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At least one organic or inorganic sulphur compound may optionally be fed along with hydrogen or with the feed to achieve the desired sulphur content. The inorganic sulphur compound can be for example H₂S or elemental sulphur or the sulphur compound may be an easily decomposable organic sulphur compound such as dimethyl disulphide, carbon disulfide and butyl thiol or a mixture of easily

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- 5 decomposable organic sulphur compounds. It is also possible to use refinery gas or liquid streams containing decomposable sulphur compounds.

In the hydrotreatment/hydrodeoxygenation step, known hydrogenation catalysts containing metals from Group VIII and/or VIB of the Periodic System may be
10 used. Preferably, the hydrogenation catalysts are supported Pd, Pt, Ni, NiMo or a CoMo catalyst, the support being alumina and/or silica, as described for instance in FI 100248. Typically, NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts are used.

In order to control the increase of temperature resulting from the aforementioned
15 reactions over catalyst beds and side reaction formation, an improved reactor configuration is presented in Figure 1. The hydrotreatment section comprises one or more catalyst beds in series, dilution agent introduction on the top of the first catalyst bed and fresh feed, recycle liquid and hydrogen introduction on top of each catalyst beds. If the dilution agent is product recycle, the product
20 recycle/fresh oil-ratio is from 5-30:1, preferably 10-30:1 and most preferably 12-25:1. The catalyst beds can be located in same pressure vessel or each bed in a separate pressure vessel. Hydrogen is fed in excess to the theoretical chemical hydrogen consumption and the feedstock is converted totally or almost totally within each catalyst bed. Using these procedures, harmful, partially converted
25 product intermediates are avoided, the temperature needed for reaction initiation is achieved in the beginning of each catalyst bed, the rise of reaction heating is controlled in the catalyst beds and the catalyst life is improved considerably.

Hydrodeoxygenation of triglycerides facilitates controlled decomposition of the
30 triglyceride molecule contrary to uncontrolled cracking. Double bonds are also hydrogenated during the controlled hydrotreatment. Light hydrocarbons and gases formed, mainly propane, water, CO₂, CO, H₂S and NH₃ are removed from the hydrotreated product.

5 It was surprisingly observed in examples that product recycle dilution can prevent or remarkably decrease the reactions between free fatty acids and the formation of high molecular weight compounds during hydrotreating, when at least 5:1 (product recycle):(fresh oil)-ratio was used. The effect of product recycle is based on two phenomena: dilution effect of recycle and more controllable and reduced
10 reaction temperatures used over catalyst bed during hydrodeoxygenation. Higher temperatures and especially hot spots of catalyst bed promote ketonisation reactions. Due to this invention, it is possible to use various sources of bio oils and fats without the need to remove fatty acids. After the hydrotreatment step, the product is subjected to an isomerization step.

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Isomerisation of n-paraffins formed during hydrotreatment

In the second step of the process, i.e. in the isomerization step, isomerization is carried out which causes branching of the hydrocarbon chain and results in
20 improved performance of the product oil at low temperatures. The isomerisation produces predominantly methyl branches. The severity of isomerisation conditions and choice of catalyst controls the amount of methyl branches formed and their distance from each other and therefore cold properties of bio diesel fraction produced. The product obtained from the hydrotreatment step is
25 isomerised under isomerisation conditions with an isomerisation catalyst.

In the process according to the invention, the feed into the isomerisation reactor is a mixture of pure n-paraffins and the composition of it can be predicted from the fatty acid distribution of individual bio oils. During the hydrotreating step of the
30 process, triglyceride oils and other fatty acid derivatives and fatty acids are almost theoretically converted to n-paraffins. Additionally propane is formed from the glycerol part of triglycerides, water and CO_x from carboxylic oxygen, H₂S from organic sulphur compounds and NH₃ from organic nitrogen compounds. It is substantial for the process that these gas phase impurities are removed as

- 5 completely as possible before the hydrocarbons are contacted with the isomerization catalyst.

The isomerization step may comprise an optional stripping step, wherein the reaction product from the hydrotreatment step may be purified by stripping with
10 water vapour or a suitable gas such as light hydrocarbon, nitrogen or hydrogen. The optional stripping step is carried out in counter-current manner in a unit upstream of the isomerization catalyst, wherein the gas and liquid are contacted with each other, or before the actual isomerization reactor in a separate stripping unit utilizing the counter-current principle.

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In the isomerisation step, the pressure varies in the range of 20-150 bar, preferably in the range of 30-100 bar and the temperature varies between 200 and 500 °C, preferably between 280 and 400 °C.

- 20 In the isomerisation step, isomerisation catalysts known in the art may be used. Suitable isomerisation catalysts contain a molecular sieve and/or a metal selected from Group VIII of the Periodic Table and/or a carrier. Preferably, the isomerisation catalyst contains SAPO-11 or SAPO-41 or ZSM-22 or ZSM-23 or ferrierite and Pt, Pd or Ni and Al₂O₃ or SiO₂. Typical isomerization catalysts are,
25 for example, Pt/SAPO-11/Al₂O₃, Pt/ZSM-22/Al₂O₃, Pt/ZSM-23/Al₂O₃ and Pt/SAPO-11/SiO₂. Most of these catalysts require the presence of hydrogen to reduce the catalyst deactivation.

- An isomerised product, which is a mixture of branched hydrocarbons and
30 preferably branched paraffins boiling in the range of 180 – 350°C, the diesel fuel range, and having one carbon atom less than the original fatty acid chain, is obtained. Additionally some gasoline and gas may be obtained.

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5 Advantages of the invention

The invention provides a method for reducing the formation of higher molecular weight compounds during the hydrotreatment of a feed obtained from plant oils and animal fats and which may contain free fatty acids.

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It was surprisingly found that the problems of prior art processes may be avoided or at least significantly reduced by the improved process according to the invention, comprising a hydrotreatment step and an isomerisation step wherein product recycle or another dilution agent in the hydrotreatment step in
15 combination with reduced operation temperature result in important improvements, particularly when the fresh feed contains more than 5 wt% of free fatty acids. A special reactor configuration and high dilution of fresh feed introduced into hydrotreatment are used in the method. The extent of side reactions is decreased and the stability of catalyst during hydrotreating is
20 increased during the hydrotreatment step.

In the examples it was be seen that the ratio of at least 5:1 (recycle:fresh) significantly decreased the formation of high molecular weight products, when the feedstock contains 10 wt-% of free fatty acids (calculated from fresh oil) is
25 used. Using at least 5:1 recycle ratio and reduced reaction temperature, free fatty acids can be processed without the need for deacidification. High quality hydrocarbons are obtained, suitable for the diesel fuel pool with high yield.

The invention is illustrated in the following with examples presenting some
30 preferable embodiments of the invention. However, it is evident to a man skilled in the art that the scope of the invention is not meant to be limited to these examples.

Examples

35 All hydrotreatment tests were performed in the presence of hydrogen.

5 **Example 1. Comparative example**

Tall oil feed (100 % free fatty acids) without product recycle

Hydrotreating of tall oil (100 % free fatty acids) with NiMo catalyst was carried out at 50 bars pressure, LHSV 1.5 and reaction temperatures from 340-360°C
10 without product recycle. Hydrogen oil ratio was 900 normal liters H₂ per liter oil fed. The hydrotreating of tall oil 100 % free fatty acid feed caused rapid deactivation of NiMo catalyst, and formation of heavy weight compounds and aromatics was observed. Bromine indexes increased during the run even if temperature compensation of catalyst was used (Figure 8). Product oil contained
15 about 7 wt-% aromatics and about 7 wt-% heavies (>375°C boiling). Density (50°C) of product oil was high 777.1 kg/m³ compared to typical values with rapeseed oil hydrotreated product oil (761-762 kg/m³) using lower reaction temperature and optimized reaction conditions.

20 **Example 2. Comparative example**

Tall oil fatty acid feed (100% FFA) at high reaction temperatures without product recycle

Hydrotreating of tall oil fatty acid feed (100% FFA) at high reaction temperatures
25 370-385°C was carried out without product recycle. Rapid deactivation of NiMo catalyst and formation of heavy weight compounds and aromatics was observed. Density of hydrotreated oil (table 1) was significantly higher than in rapeseed oil runs (typically 761-762 kg/m³). Both oils contained mainly C18 fatty acids (~90-wt-%) and rather steady formation of water was observed during run. During the
30 tall oil hydrotreating about 7-8 wt-% heavier molecular weight compounds and 8.1 wt-% aromatics were formed. These side reactions are caused by concentrated fatty acid feed and too high reaction temperatures. Deactivation of catalyst is clearly seen from increasing bromine indexes. During the satisfactory operation bromine index should be below 50. Table 1 describes densities, bromine indexes,
35 reaction temperatures and water formed during test runs for 2 to 14 days using tall oil fatty acid feed (100% FFA) without recycling.

5 Table 1.

Duration of test run	2nd day	4th day	6th day	9th day	11th day	12th day	13th day	14th day
Temperature, °C	370	375	378	381	385	385	385	385
Density, 50°C, kg/m ³	771.8	773.1	773.7	776.5	779.1	779.8	780.5	781.2
Bromine index	101	150	188	198	247	269	300	330
Product water, %	9.37	9.5	9.81	10.3	10.2	10.0	10.1	10.2

Example 3. (Comparative example)**Effect of metal impurities of bio oils on the catalyst performance**

- 10 Tube reactor hydrotreatment test runs were carried out using crude rapeseed oil, crude animal fat and purified rapeseed oil. Analysis of these feeds are shown in Table 2. Crude feeds contained significant amount of metals, organic phosphorus, sulphur and nitrogen compounds. Purified feeds contained only trace levels of these impurities

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Table 2. Impurity levels of crude and purified plant oils and animal fats

Impurity	Unit	Crude Rapeseed oil	Purified Rapeseed oil	Crude Animal fat
Metals (total)	ppm	90	~ 0	162
Org.nitrogen	ppm	33	7.2	1125
Free Fatty acid, GPC	Wt-%	0.8	0.7	10.8
Total Acid Number	mg KOH/g	1.0	0.1	21.5
Phosphorous	ppm	110	<1	86
Sulphur (original)	ppm	3	1	85

5 Test runs using crude, unpurified oils/fats showed that catalyst needed higher temperatures to work properly, but gradually lost its activity (Figure 5). Triglycerides and increased bromine number of product oil was found. High amount of metals were also detected on to the catalyst. Temperature profile of the catalyst bed showed that top of the catalyst bed was deactivated and reaction
10 section moved forward (Figure 4), when reactor heating was maintained steady. Metals adsorbed on to the catalyst also promote side reactions like decarb-reactions.

First hydrotreatment test run was carried out using crude rapeseed oil. Purified
15 rapeseed oil was used as a reference feed. Purified rapeseed oil achieved complete HDO conversion at 305°C using WHSV=2. Crude rapeseed oil gave total HDO conversion not until reaction temperature 330°C was used with space velocity WHSV=1. It was however seen from temperature profiles over the catalyst bed that first part of catalyst was deactivated very quickly. In Figure 4, reaction
20 temperature profile over catalyst bed and performance of crude rapeseed oil are presented.

Second hydrotreatment test run was carried out using purified rapeseed oil and crude animal fat. Purified rapeseed oil was used as a reference feed. Purified
25 rapeseed oil with product recycle achieved complete HDO conversion at 305°C using WHSV=1. Crude animal fat with product recycle did not give complete HDO conversion at 305°C using WHSV=1. It was seen from GPC analyses that product oil contained triglycerides and catalyst also significantly deactivated during crude animal fat feed. Pumping problems was also observed during crude
30 animal fat feeding. Performance of crude animal fat is presented in Figure 5.

Example 4. (Comparative example)

Effect of free fatty acids (10 wt-% in fresh feed) on the formation of high molecular weight hydrocarbons

5 Hydrotreatment was carried out using purified rapeseed oil as reference feed without product recycle. A test run was carried out at 305°C and 50 bars pressure using WHSV= 1 and H₂/oil-ratio=1000. Sulphur content of feed was 570 ppm. During a second hydrotreatment test period stearic acid was fed (10 wt-% from rapeseed oil) along with purified rapeseed oil using same reaction conditions
10 without product recycle. It was right away observed that the extent of high molecular weight compounds increased gradually from initial level ~3 wt-% to ~8 wt-%. These higher molecular weight compounds (molecular weight double or more of the feed) are not in the boiling range of diesel fuel and thus decrease diesel yield and potentially shorten the catalyst life. Thus free fatty acids in bio
15 oils make their processing more difficult. In Figure 2 the increase of formation of high molecular weight hydrocarbons is observed, when 10 wt-% free fatty acids was fed along with purified rapeseed oil triglycerides without product recycle.

Example 5.

20 Effect of product recycle on preventing formation of unwanted heavy side reaction compounds when the feed contained 10 wt-% free fatty acids

A hydrotreatment test run was carried out using 10 wt-% stearic acid containing purified rapeseed oil as reference feed without product recycle under following
25 reaction conditions: WHSV= 1, 50 bars, 305°C, H₂/oil-ratio=1000 and sulphur content of feed =570 ppm. During the second hydrotreatment test run period same feed was diluted with product hydrocarbons so that (fresh oil) / (product recycle) - ratio was 1:5. WHSV of fresh oil was maintained at 1, therefore WHSV of total oil feed increased to 6. The reaction temperature was kept at 305°C and reaction
30 pressure at 50 bars. H₂/(fresh oil)-ratio was maintained at 1000. HDO product (n-paraffins) simulated product recycle, which was mixed in advance with fresh oil. The initial content of heavy hydrocarbons in the recycle was ~0,4 wt-%.

It was unexpectedly observed that the formation of heavy hydrocarbons was
35 almost totally prevented or at least very significantly decreased when product

5 recycle was used (Figure 3). This is most probably caused by significantly diminished side reactions of free fatty acids wherein a carboxylic acid molecule can react with another carboxylic acid molecule to form a higher molecular weight compounds. In Figure 3 the effect of product recycle on preventing the formation of unwanted higher molecular weight by-product is presented. Table 3
10 presents analysis results of the feed and products.

Table 3. Analysis results of the feed and products

Property	Method	Units	Feed analyses				Product analyses		
			AR	Recycle feed	AR (10% SA)	AR (10% SA) + REC 1: 5	AR + 10 wt-% stearic acid without recycle	AR + 10 wt-% SA + Recycle after 196 hours	AR + 10 wt-% SA + Recycle after 552 hours
Density, 15°C calc.	D 4052	kg / m ³	920.4	788.1	915.8	807.2	790.8	788.3	788.3
Density, 50°C	D 4053	kg / m ³	897.6	761.4	893.2	781.2	764.2	761.7	761.7
Br-index	D 2710	mg/100 g		53.7			21.5		26
Br number	D 1159	g/100 g	56		49.1	6.3			
Iodinenumber	D 5554	g/100 g	112		103	18			
HC	GPC	area-%		99.6		83.0	94.3	99.6	99.6
Fatty acids	GPC	area-%	0.7	0	10.6	1.8	0	0	0
Heavy HC	GPC	area-%	0	0.4		0.5	5.7	0.4	0.4
Diglycerides	GPC	area-%	2.3	0	2.4		0	0	0
Triglycerides	GPC	area-%	97	0	87	14.7	0	0	0

15 SA = Stearic acid, AR = purified rapeseed oil, REC = product recycle, HC = hydrocarbons, heavy HC = high molecular weight hydrocarbons

Example 6. (Comparative example)

The effect of lower reaction temperature on the selectivity of n-paraffins and oil yield

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Studies were carried out with NiMo catalyst using rapeseed oil as feed and reaction temperatures 280-330°C and 340-360°C, WHSV=1 and reactor pressure

- 5 of 50 bars. Alkali raffinated rapeseed oil triglycerides contained mainly C₁₈ fatty acids. C₁₈ fatty acids contributed about 89 wt-% of all fatty acids in rapeseed oil. Theoretical amount of n-paraffins formed from rapeseed oil fed is about 86.4 wt-% (calculated from rapeseed oil fed).
- 10 Complete HDO conversion with almost theoretical n-paraffin yield was accomplished, when well controlled reaction temperatures <330°C were used. Almost theoretical n-paraffin yields tell us from complete HDO conversion and very controllable operation without significant side reactions. High amount of side reactions (cyclisation, aromatisation and cracking) and low n-paraffin yield were
- 15 observed when unnecessary high reaction temperatures 340-360°C was used. In Figure 6 the conversion of rapeseed oil triglycerides to n-paraffins is presented.

Example 7.

Stability of catalyst

- 20 The stability of NiMo-catalyst using palm oil model feed (impurities added) along with product recycle (catalyst life test) was carried out using following reaction conditions: Reaction temperature = 300-305°C, Reactor pressure = 40 bars, WHSV (fresh) = 0,5, WHSV (total) = 3, H₂/Oil (fresh) = 900, Sulphur in feed =
- 25 100 w-ppm. Palm oil was used as a main component of feed, but it was modified with animal fat, fractions of free fatty acids, crude rapeseed oil, and lecithin in order to get suitable specification of impurities of test feed. Fresh feed analysis is presented below in table 4. Fresh oil was then diluted in advance with 1:5 ratio of HDO product (simulates product recycle). The duration of test run was over 9
- 30 months. Stable operation was maintained (table 4 and Figure 7) and the formation of heavies was steady over the whole test run Figure 7.

5 Table 4. Stability of catalyst

Run duration			Fresh Feed analysis	Product oil analysis			
				383 hours	1898 hours	3408 hours	5601 hours
Analysis	Method	Unit					
Density, 15°C	D 4052	kg / m ³	804.9	787.4	785.6	785.3	784.9
Density, 50°C	D 4052	kg / m ³	778.8	760.7	758.9	758.6	758.1
Br-index	D 2710	mg/100 g	29200	33	48	33	11
HC	GPC	area-%	0	99.3	99.4	99.3	99.4
Fatty acids	GPC	area-%	1.2	0	0	0	0
Monoglyc/high molec. weight HC	GPC	area-%	0.3	0.7	0.6	0.7	0.6
Diglycerides	GPC	area-%	6.3	0	0	0	0
Triglycerides	GPC	area-%	92.1	0	0	0	0
TAN	D664	mg KOH/g	2.1	~0	~0	~0	~0
Sulphur	D 5453	ppm	3	1.2	2.0	2.7	2
Nitrogen	D4629	mg/kg	6	<1	<1	1.2	<1
Sodium, oil	AAS	mg/kg	3	0.4	<0.1	<0.1	<0.1
Calcium, oil	AAS	mg/kg	2	0.3	<0.1	<0.1	<0.1
Magnesium, oil	AAS	mg/kg	0.3	<0.1	<0.1	<0.1	<0.1
Molybdenum, oil	AAS	mg/kg	-	<0.5	<0.5	<0.5	<0.5
Aluminum, oil	ICP metals	mg/kg	<2	<2	<2	<2	<2
Iron, oil	ICP metals	mg/kg	<1	<1	<1	<1	<1
Nickel, oil	ICP metals	mg/kg	<1	<1	<1	<1	<1
Phosphorus, oil	ICP metals	mg/kg	4	<1	<1	<1	<1

5 Claims

1. Process for the manufacture of diesel range hydrocarbons wherein a feed is hydrotreated in a hydrotreating step and isomerised in an isomerisation step, **characterized** in that a feed comprising fresh feed containing more than 5 wt% of free fatty acids and at least one diluting agent is hydrotreated at a reaction temperature of 200-400°C, in a hydrotreating reactor in the presence of catalyst, and the ratio of the dilution agent/fresh feed is 5 – 30:1.
2. A process according to claim 1, **characterised** in that the feed contains more than 10 wt% of free fatty acids.
3. A process according to claim 1 or 2, **characterised** in that in the hydrotreating step the reaction temperature is 250-350°C, preferably 280-340°C.
4. A process according to any one of claims 1 - 3, **characterised** in that the dilution agent is selected from hydrocarbons and recycled products of the process or mixtures thereof.
5. A process according to any one of claims 1 – 4, **characterised** in that the feed contains less than 10w-ppm alkaline and alkaline earth metals, calculated as elemental alkaline and alkaline earth metals, less than 10w-ppm other metals, calculated as elemental metals, and less than 30w-ppm phosphorus, calculated as elemental phosphorus.
6. A process according to any one of claims 1 - 5, **characterised** in that the diluting agent:fresh feed ratio is 10-30:1 preferably 12-25:1.

- 5 7. A process according to any one of claims 1 - 6, **characterised** in that the
 feed contains 50-20000 w-ppm of sulphur, calculated as elemental
 sulphur.
- 10 8. A process according to any one of claims 1 - 6, **characterised** in that the
 fresh feed is of biological origin, selected from plant oils/fats, animal
 fats/oils, fish fats/oils, fats contained in plants bred by means of gene
 manipulation, recycled fats of the food industry and mixtures thereof.
- 15 9. A process according to any one of claims 1 - 7, **characterized** in that the
 fresh feed is selected from rapeseed oil, colza oil, canola oil, tall oil,
 sunflower oil, soybean oil, hempseed oil, olive oil, linseed oil, mustard oil,
 palm oil, peanut oil, castor oil, coconut oil, lard, tallow, train oil or fats
 contained in milk.
- 20 10. A process according to any one of claims 1 - 9, **characterized** in that a
 mixture of feed of biological origin and a hydrocarbon/hydrocarbons is
 used as the fresh feed.
- 25 11. Process according to any one of claims 1 - 10, **characterized** in that the
 hydrotreating catalyst bed system comprises one or more catalyst beds.
12. Process according to any one of claims 1 - 11, **characterized** in that in the
 hydrotreating step pressure varies in the range of 20-150 bar, preferably in
 the range of 30-100 bar.
- 30 13. Process according to any one of claims 1-12, **characterized** in that in the
 isomerisation step pressure varies in the range of 2-15 MPa, preferably in
 the range of 3-10 MPa, the temperature varying between 200 and 500 °C,
 preferably between 280 and 400 °C.
- 35

- 5 14. Process according to any one of claims 1 – 13, **characterized** in that the hydrotreating is carried out in the presence of a hydrogenation catalyst, said hydrogenation catalyst containing a metal from the Group VIII and/or VIB of the Periodic System.
- 10 15. Process according to claim 20, **characterized** in that the hydrotreating catalyst is a supported Pd, Pt, Ni, NiMo or a CoMo catalyst, the support being alumina and/or silica.
- 15 16. Process according to any one of claims 1 - 15, **characterized** in that an isomerization catalyst containing molecular sieve is used in the isomerization step.
- 20 17. Process according to claim 16, **characterized** in that the isomerization catalyst contains a metal from the Element Group VIII.
- 25 18. Process according to claim 16 or 17, **characterized** in that the isomerization catalyst contains Al_2O_3 or SiO_2 .
19. Process according to any one of claims 16 - 18, **characterized** in that the isomerization catalyst contains SAPO-11 or SAPO-41 or ZSM-22 or ZSM-23 or ferrierite and Pt or Pd or Ni and Al_2O_3 or SiO_2 .